

REDUCTION OF N-ALKYLPYRIDINIUM CATIONS AT MERCURY ELECTRODES

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Received September 1st, 1970

In addition to classical polarography, the studied N-alkylpyridinium salts (from CH_3 to $n\text{-C}_5\text{H}_{11}$) were subject to coulometric and microcoulometric measurements, to experiments with periodically changed square-wave voltage, to polarography with superimposed ac. voltage, to single-sweep and multi-sweep polarography *etc.* The obtained results enabled a novel, more precise interpretation of their reduction, initiated by the formation of a radical which rapidly dimerises. Coulometric measurements in absence and in presence of ascorbic acid revealed the role of the follow-up chemical and electrochemical reactions.

As the simplest and relatively easily accessible pyridine derivatives — and evidently also with regard to their relationship to nicotinamide-adenine-dinucleotide — the N-alkylpyridinium salts have been several times studied by means of polarography^{1,2}. Mairanovskii³ suggested a reduction mechanism. However, up to now the polarographic experiments have been carried out under different conditions by various authors so that the results for N-alkylpyridinium salts with different alkyl substituents are usually not comparable. This is why we made an investigation in the homologous series of N-alkylpyridinium iodides with alkyl substituents from CH_3 to $n\text{-C}_5\text{H}_{11}$ (all with an unbranched chain). All of them were prepared by us.

EXPERIMENTAL

Polarographic measurements were carried out with a LP 60 polarograph (Laboratorní přístroje, Prague) in cells constructed in the laboratories of this Institute. Controlled current oscillographic measurements were performed with a Polaroscope LP 600 (Laboratorní přístroje, Prague). Oscillographic polarography with applied voltage was carried out making use of triangular voltage sweeps delivered by a pulse generator constructed in the workshops of this Institute.

The adsorptivity of the substances studied in this paper was investigated by means of polarography with superimposed ac. voltage according to Breyer, making use of the Polarecord E 261 Metrohm with an ac. modulator. Coulometric measurements were made with the electronic integrator Amel 558. The drop-time was controlled by an automatic drop-time tapper (Tesla, Pardubice).

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RESULTS

Classical Polarography with the Dropping Mercury Electrode. In spite of the simple structure of N-alkylpyridinium salts their polarographic investigation is met with a number of complications, in particular by their strong adsorption from aqueous solutions on mercury. This is why some experiments were run at rather high concentrations of non-aqueous solvents and the composition of the electrolyte is referred to in the respective place of the text. The dependence of the polarographic behaviour on pH cannot be presented. In buffered solutions of $\text{pH} < 10$ (most experiments were carried out with Britton-Robinson buffers) the waves of all five quaternary cations are overlapped by the wave of hydrogen ion reduction from the supporting electrolyte. Only in the region of $\text{pH} 10\text{--}12$ the reduction proceeds in a single, relatively negative wave whose half-wave potential and limiting current are pH-independent. At $\text{pH} > 12$ (NaOH) the wave gradually disappears with time because the depolariser is decomposed. The waves can be best followed in the most alkaline Britton-Robinson buffers. A characteristic feature of the polarographic behaviour of all five cations is the formation of streaming maxima which can be only with difficulty suppressed. Mairanovskii's interpretation^{3,4} of their origin is based on the formation of an insoluble reduction product. This results in a non-uniform coverage of the mercury drop and, accordingly, in a non-uniform surface tension σ ; this leads to a tangential motion which transports further depolariser and does not stop earlier than on the limiting current.

The influence of the alkyl substituent on the half-wave potential (after suppressing the maximum with gelatin) follows from the subsequent experimental values (Britton-Robinson buffer $\text{pH} 11.9$, 75% dimethyl sulfoxide, $4 \cdot 10^{-4}\text{M}$ depolarizer, E vs S.C.E.):

N-alkyl	methyl	ethyl	n-propyl	n-butyl	n-pentyl
$E_{1/2}, \text{V}$	-1.27	-1.28 ₅	-1.29 ₅	-1.30	-1.32

The wave height is a linear function of concentration over the region $5 \cdot 10^{-5}$ to 10^{-3}M . Sharp streaming maxima appearing at low concentrations of non-aqueous solvents can be only suppressed when working with low depolariser concentrations and adding gelatin. With 10^{-4}M depolariser in Britton-Robinson buffer $\text{pH} 11.9$ and 20% dimethylformamide the following half-wave potentials were observed (volts vs S.C.E.): methyl -1.48, ethyl -1.47₅, n-propyl -1.46.

Thus the shift in this medium is just in the reverse order than in the solution with 75% dimethyl sulfoxide.

The log plots could be only evaluated for the above three solutions:

Straight lines were obtained in the coordinates $\log [i^{2/3}/(i_d - i)] i^{1/3} = f(E)$ (Fig. 1) with inversed slopes 56.5 mV for N-methylpyridinium iodide, 53 mV for N-ethylpyridinium iodide and 65 mV for N-n-propylpyridinium iodide.

Further the dependence of the half-wave potentials $E_{1/2}$ on drop-time t_1 with a controlled drop-time (from 0.5 to 4.0 s), again at $\text{pH} 11.9$ with 10^{-4}M depolarizer and in presence of gelatin, was investigated. If the drop-time is decreased by one order a linear shift to more negative potentials follows from the graphs; this amounts to 25 mV in N-methyl, to 27 mV in N-ethyl, to 33 mV in N-n-propyl, to 34.5 mV

in N-n-butyl, and to 35 mV in N-n-pentyl. These values somewhat differ from those published by Mairanovskii² for the N-methylpyridinium cation (33 mV).

Curves with Superimposed ac. Voltage

The curves depicting the alternating current as a function of potential⁵ in presence of depolariser were compared with those of the blank. In all substances adsorption of the oxidised form was found. This effect can be followed on polarograms (Fig. 2) where the curve of the solution containing the depolariser passes below that of the supporting electrolyte alone. The observed lowering of the ac. current on the curves in the potential regions before the reduction starts increases in all substances with concentration; however, in the three highest derivatives the surface of the dropping mercury electrode is soon saturated and the decrease does not further change with increasing concentration. Since in the N-n-propyl derivative the saturation is attained at a $5 \cdot 10^{-4}M$ concentration and in the N-n-butyl and N-n-pentyl cation at $2-3 \cdot 10^{-4}M$, it is not easy to decide how the degree of adsorption varies with the length of the carbon chain on the nitrogen atom.

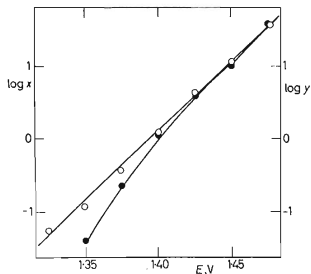


FIG. 1

Logarithmic analysis of the wave for $2.5 \cdot 10^{-4}M$ N-ethylpyridinium iodide

Britton-Robinson buffer pH 11.12, $5 \cdot 10^{-3}\%$ gelatin. $\log y = f(E)$ where $y = \frac{i}{i_d - i}$; $\log x = f(E)$ where $x = \frac{i}{i_d - i}$. $i \cdot i^{1/3}$.

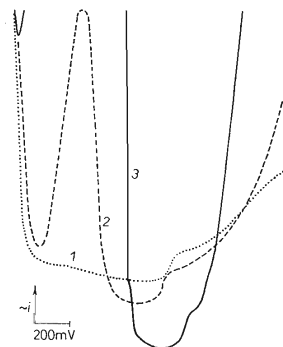


FIG. 2

a.c.-Polarogram of N-methylpyridinium Iodide in Britton-Robinson Buffer

From $-0.5 V$, $\Delta E 50 mV$. Concentration of N-methylpyridinium iodide: 1 0 (supporting electrolyte alone), $2.1 \cdot 10^{-4}M$, $3.1 \cdot 10^{-3}M$.

Coulometry with a Dropping Mercury Electrode

Since the main aim of this communication is the determination of reduction mechanisms in N-alkylpyridium cations, in particular as regards the follow-up reactions, we had first to determine the number of electron consumed per molecule of the studied substance. Coulometry with a dropping mercury electrode at a constant potential (maintained by a polarograph) corresponds most closely to the polarographic conditions if the volume is small and concentration low (1 ml, $5 \cdot 10^{-4}$ M). The electrolysis lasts several hours and its course is followed by recording polarographic curves in regular intervals. The evaluation is performed by using the following equation⁶:

$$\log i_1^0 - \log i_1 = \frac{i_1^0 \cdot t}{2.3 F n C_{t=0} V},$$

where i_1^0 is the limiting current at $t = 0$, i_1 limiting current at time t , F Faraday constant, $C_{t=0}$ the concentration for the time $t = 0$ (expressed in mol l^{-1} , V volume of the solution in l , t time. In practice the logarithm of the limiting diffusion-controlled current during electrolysis is plotted vs time. From the slope of the straight line thus obtained the value of n is calculated. The method is relatively simple but is encumbered with a considerable error because of depletion of the solution around the electrode.

The values obtained with $5 \cdot 10^{-4}$ M solutions in Britton–Robinson buffers pH 11.95 at $E - 1.5$ V (in the region of the polarographic maximum) are as follows:

N-alkyl	methyl	ethyl	n-propyl	n-butyl	n-pentyl
n	1.28	1.21	0.97	0.99	0.81

In addition to the usual error of the method, these results are affected also by the fact that coulometry was not carried out at the potential of the limiting current but at the potential of the maximum. Otherwise anomalies would occur at the beginning of the electrolysis. In the first two homologues the values of D obtained from the Ilkovič equation basing on values of n thus determined are quite plausible and lie in the region of $9 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

Coulometry with a Mercury Pool Electrode

Coulometric measurements carried out with a stirred mercury pool electrode correspond much better to the conditions of a preparative electrolysis. The electrolyses were run with 10^{-3} M N-alkylpyridinium salts at pH 11.9. The reduction potentials were chosen on the limiting current of the polarographic reduction waves (with the first two derivatives they were -1.8 V, with the third one -1.85 V, and with the last two -1.9 V). The following values of n were obtained:

N-alkyl	methyl	ethyl	n-propyl	n-butyl	n-pentyl
n	3.19	2.36	1.26	1.37	1.27

In these measurements, the higher values of n are conspicuous as compared to those obtained with the dropping mercury electrode. The interpretation is based on the fact that on the dropping electrode a polarographic current is recorded which is due only to the reduction of cations that diffuse to the electrode. Taking not into account a transfer of concentration polarisation, the value of n – with regard to a slow follow-up reaction, *i.e.* to dimerisation of the radical thus formed – should be equal to one. Owing to experimental errors and to the relatively high rate of dimerisation in the lower homologues, the measured values range from 1.2 to 1.3 in the methyl and ethyl derivatives. When working with a large-area mercury pool electrode – the electrolysis may last several hours – the products of dimerisation are subject to further reduction since they are electroactive at the given potential; consequently the experimental value of n is increased and is not identical with n for the primary reduction process visible *e.g.* in classical polarography. As follows from the results both with the mercury-pool electrode and with the dropping mercury electrode the dimerisation proceeds very rapidly with the methyl and the ethyl derivative.

⁵ In order to stop the electrode process immediately after the transfer of the first electron and to hinder the follow-up chemical reactions we attempted to react the primary radical with a suitable reagent. In the literature^{7,8} carbon dioxide, methyl iodide and methyl bromide are recommended to this purpose. However, these compounds did not prove convenient in our experiments; carbon dioxide, *e.g.*, makes the solution acidic and the reduction wave studied in its presence is overlapped by a hydrogen wave. After 10 minutes of electrolysis one can observe the formation of an anodic wave which could correspond to the oxidation of the product of a reaction between the primary radical and CO_2 . A serious drawback in the use of methyl bromide and methyl iodide is their poor solubility in water.

Ascorbic acid proved to be a very advantageous reagent⁹. Its stability in alkaline solutions in the course of 20–30 min was confirmed by polarography (in presence of N-methylpyridinium iodide; both with 10^{-3}M solutions). The possibility of electrolysis and of coulometric measurements was checked by polarographically monitoring the electrolysis of 10^{-3}M N-methylpyridinium iodide in a Britton–Robinson buffer pH 11.9 in presence of 10^{-3}M ascorbic acid at -1.65 V . This electrolysis was carried out at a stirred mercury-pool electrode. A polarogram was recorded before electrolysis and further curves in 10 min intervals. A decrease of the wave-heights was observed both for the studied substance and for ascorbic acid (Fig. 3). The anodic wave of ascorbic acid, however, decreases approximately twice as much as the cathodic wave of the N-methylpyridinium cation. Experiments with solutions containing the N-methylpyridinium cation and ascorbic acid and making use of the Kalousek commutator did not result in the formation of new waves as compared to the solutions without ascorbic acid. The coulometric measurements carried out at a stirred mercury-pool electrode in presence of ascorbic acid (10^{-3}M depolariser, 10^{-3}M ascorbic acid, pH 11.9) yielded the following results:

N-alkyl	methyl	ethyl	n-propyl	n-butyl	n-pentyl
<i>n</i>	1.60	1.42	0.96	1.03	0.97

The values of *n* are substantially different from those obtained without blocking. They also point to the fact that the dimerisation of small radicals (N-methyl, N-ethyl) in which the sterical hindrance is negligible occurs so rapidly that it competes with the reaction with ascorbic acid.

Experiments with a Hanging Mercury Drop

The current-voltage curves with the hanging mercury drop were registered mainly in order to see how the curves are influenced by the reduction products in repeated recordings on the same drop. This is important *e.g.* in planning preparative electrolyses with large area mercury electrodes. The curves were recorded three times with the same drop; in all cases two different voltage ranges were made use of: from -1.0 V to -2.0 V, and from -0.5 V to -2.0 V and back to -0.5 V.

All five cations reduce in a single peak which shifts to less negative potentials with longer alkyl chains (10^{-3} M depolariser, pH 11.9):

N-alkyl	methyl	ethyl	n-propyl	n-butyl	n-pentyl
E_p , V	-1.47	-1.45	-1.48	-1.46	-1.45

In the three higher derivatives a further peak has been observed at more negative potentials (-1.88 V), probably of catalytic origin. This catalytic peak grows gradually when repeating the registration of the curves in the N-n-propyl derivative. The catalytic reduction of hydrogen ions is probably caused by the reduction product gene-

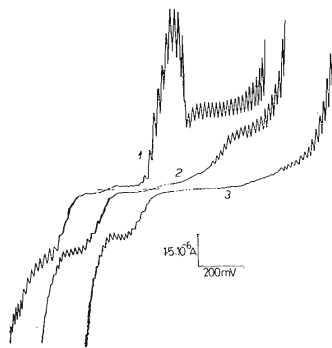


FIG. 3

Polarographic Curves during Electrolysis of 10^{-3} M N-Methylpyridinium Iodide in Britton-Robinson Buffer pH 11.5 in Presence of 10^{-3} M Ascorbic Acid

1 Before electrolysis, 2 after 10 min of electrolysis, 3 after 20 min of electrolysis. For the sake of simplicity the parts of polarographic curves (between -0.3 V and -1.1 V) where no effects are observed are not drawn here.

rated at the electrode the amount of which increases during electrolysis. In the *n*-butyl and *n*-pentyl derivative, on the other hand, the product present in a larger quantity at the electrode inhibits the catalytic current. This is in accordance with the influence of repeated registration on the more positive peak in these two substances. The catalytic peaks disappear when working with solutions containing 50% dimethyl sulfoxide. If the recording is repeated the more positive peak is lowered, E_p is slightly shifted to more negative potentials. As a whole, in the *N*-methyl derivative the individual curves somewhat differ from each other in repeated registrations, slightly more in the *N*-ethyl derivative (ΔE_p is about 20 mV). In the remaining three homologues a strong decrease in the peak-height is observed if the registration on the same drop is repeated.

The behaviour of the compounds is different if the polarograms are recorded from -0.5 V to -2.0 V and back to -0.5 V. In essence, the curve obtained by recording from -0.5 V to more negative potentials is the same as that described above, *i.e.* with the normal reduction peak and with the catalytic one. The difference only appears during the registration toward less negative potentials (Fig. 4). An exception is *N*-methylpyridinium iodide where a wave appears between -1.6 V and -1.4 V. In the cations from *N*-C₂H₅ to *N*-*n*-C₃H₁₁, a distinct anodic peak forms at strongly

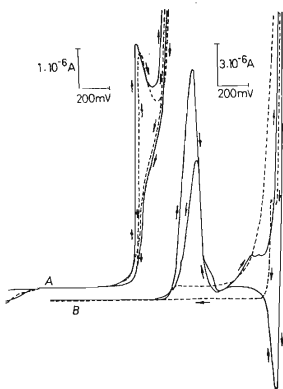


FIG. 4

Reduction of 10^{-3} M *N*-alkylpyridinium Cations in 10 ml Britton-Robinson Buffer pH 11.9 at a Hanging Mercury Drop Electrode

On the same drop two curves have been always recorded from -0.4 V to -2.0 V and back to -0.4 V. A *N*-methyl, B *N*-*n*-pentyl; first curves: full line, second curves: dashed line.

negative potentials ($E = -1.8$ – -1.9 V); in view of the potential region and its increase during the accumulation of the product one cannot decide definitely whether this peak is of capacity origin (due to desorption of the product) or whether it corresponds to a reoxidation of the adsorbed product¹⁰. At less negative potentials the shape of the curve is similar to that of the N-methyl derivative. In the N-n-C₄H₉ and N-n-C₅H₁₁ derivatives, the small wave obtained in the polarisation to less negative potentials is deformed by a maximum. This maximum is similar to that observed on single- and multi-sweep polarograms after an accumulation of the product at -1.8 V and with a periodic pulse from -1.8 V to -1.0 V (sweep rate 1 V s^{-1}). In the potential range where the main reduction peak forms an acute cathodic maximum has been observed in the registration from -1.8 V to -1.0 V; it is particularly characteristic of the first curve in the homologues with a longer aliphatic chain.

Experiments with Periodically Changed Rectangular Voltage (Kalousek Commutator)

All measurements were carried out with the circuit¹¹ in which the products are generated with a constant auxiliary potential E_{aux} in the producing period and are studied in the recording period with a continually changed potential E . The dependence of commutated waves on E_{aux} , on the frequency of commutation f and on depolariser concentration c was studied; in some cases the influence of temperature on these effects was also investigated. Most experiments were carried out in Britton-Robinson buffers pH 11.9 with $5 \cdot 10^{-4} \text{ M}$ depolariser.

Dependence on E_{aux} at f 6.25 c.p.s. The auxiliary potential E_{aux} was varied between -1.4 V and -1.8 V. As soon as E_{aux} corresponds to the reduction potential of the depolariser, one, two or three waves are observed on the commutated curves, this depending on the character of the alkyl substituent. In N-methyl and N-ethylpyridinium iodide one irreversible anodic wave is observed with E_{aux} more negative than -1.5 V; its $E_{1/2}$ is shifted to more positive values as E_{aux} becomes more negative. With the N-methyl derivative it appears at -0.79 V ($E_{\text{aux}} - 1.5$ V) and at -0.76 V ($E_{\text{aux}} - 1.6$ and -1.75 V); with N-ethyl at -0.86 V ($E_{\text{aux}} - 1.6$ V) or at -0.82 V ($E_{\text{aux}} - 1.7$ V). Two anodic waves are observed on the commutated curve of N-n-propyl and N-n-butylpyridinium iodide. If E_{aux} is changed to more negative values the higher more positive shifts towards more negative values whereas just an opposite shift can be seen with the lower, more negative wave. Three anodic waves on the commutated curve have been observed with N-n-pentylpyridinium iodide. The first, most positive wave is shifted over the investigated region of potentials ($E_{\text{aux}} - 1.5$ to -1.8 V) to more negative values (-0.76 V to -0.84 V). Since the height of this wave decreases with a negative change in E_{aux} and the height and $E_{1/2}$ of the second wave remain unaffected by this change the first wave gradually coalesces with the second wave, and at $E_{\text{aux}} - 1.8$ V gives a wave with $E_{1/2} - 0.84$ V. The third, most negative wave shifts to more negative values under these conditions (-1.04 V to -1.06 V).

Whereas in the three highest derivatives several waves can be seen on the commutated polarograms, in the N-methyl and N-ethyl derivative a small maximum is observed at -1.3 V to -1.4 V (just before the transition from the anodic to the cathodic current; it disappears at lower temperatures and lower depolariser concentrations. At higher temperatures and higher concentrations it is shifted to more negative potentials, and finally forms a prewave of the reduction wave on the cathodic side. This maximum is suppressed by adding a surface-active agent or by a non-aqueous solvent: from this we conclude that it is evoked by adsorption of an electrolysis product.

Influence of switching frequency ($E_{aux} - 1.75$ V). When varying the frequency from 1.56 c.p.s. to 25 c.p.s. the half-wave potential of the main anodic wave is shifted to more positive values in all five substances. With the methyl and ethyl derivatives the total shift ΔE is 120 mV, starting from -0.77 V and -0.79 V, respectively. With the other three derivatives it is again 120 mV, starting from -0.80 V for N-n-propyl, from -0.85 V for N-n-butyl and -0.87 V for N-n-pentyl.

The small maximum which only appears in the two lower derivatives and is on the anodic side at 6.25 c.p.c. is shifted to the cathodic side by lowering the switching frequency and turns into a prewave on the cathodic reduction wave. With the higher derivatives, further, more negative anodic waves appear when increasing the frequency. In the N-propyl derivative this second wave — observed from f 6.25 c.p.s. upwards with $E_{1/2} - 1.1$ V — shifts to more negative potentials by increasing frequency and has $E_{1/2} - 1.16$ V at f 25 c.p.s. A similar behaviour has been observed with the other more negative anodic wave in the N-butyl derivative which, however, splits into two waves at 25 c.p.s. ($E_{1/2} - 1.05$ and -0.86 V). In the N-pentyl derivative two small more negative anodic waves ($E_{1/2} - 0.97$ V and -0.85 V) appear in addition to the main wave at 6.25 c.p.s. already. At higher frequencies the more negative one shifts to more negative potentials. Since the more negative anodic waves decrease at 0°C and pass into the main anodic wave at 50°C they evidently do not correspond to the electrode process of a further particle in the solution but more probably to adsorption and desorption equilibria of the reduction products.

Dependence of commutated curves on depolariser concentration. The height of the anodic wave obtained in commutation experiments with the first three homologues is a linear function of the depolariser concentration. With increasing concentration the above mentioned maximum appears (at $4 \cdot 10^{-4}\text{M}$ with the methyl and at $3 \cdot 10^{-4}\text{M}$ with the ethyl derivative). At still higher concentrations in both cases it passes into a prewave of the cathodic reduction wave. In the N-propyl derivative the more negative anodic prewave is more distinct at lower concentrations up to $2 \cdot 10^{-4}\text{M}$; in this region it also ceases to be concentration-dependent. These properties all contribute to the conception of its adsorption-controlled origin.

Temperature dependence of commutated anodic waves. The temperature dependence was followed with $5 \cdot 10^{-4}\text{M}$ solutions at pH 11.95 . The anodic wave corresponding to the oxidation of the particle which has been formed in the production period grows with increasing temperature and shifts to more negative potentials.

N-alkyl	methyl	ethyl	n-propyl	n-butyl	n-pentyl
$(E_{1/2})_{15^\circ}, \text{V}$	-0.75	-0.82	-0.83	-0.81	-0.80
$(E_{1/2})_{40^\circ}, \text{V}$	-0.88	-0.93	-0.93	-0.93	-0.90

The temperature dependence of the small adsorption maximum in the N-methyl and N-ethyl derivative and the temperature dependence of the more negative anodic waves observed in the three higher homologues have been described in the above text.

Linear Voltage Sweep Polarography

The measurements in all five salts were carried out with triangular voltage pulses (single-sweep and multi-sweep). Some features are common with all derivatives: *a*) the main cathodic peak *A* appears at about -1.6 V; *b*) the anodic peak *B* (at -0.5 or -0.6 V) which appears only if the reduction in *A* has occurred, shifts to more positive values during the life of the mercury-drop; *c*) the reversible pair of peaks (oxidation peak J_0 and reduction peak J_R) is caused by the presence of iodides in the solution and by their reaction with mercury ions.

A and *B* are the principal pair of peaks; they can be ascribed to the electrochemical processes confirmed also by other polarographic methods. In addition to this, when polarising from -1.7 V to -1.0 V and back to more negative potentials, a further, reversible pair of peaks, *C* (anodic) and *D* (cathodic), was observed with the N-methyl, N-ethyl and N-n-propyl derivative. These peaks only result with high polarisation slopes (above 10 Vs^{-1}) at approx. -1.35 V for the methyl derivative. With growing length of the aliphatic chain these peaks are shifted to less negative values. The height of the anodic peak increases by prolonged reduction (e.g. 2 s) at -1.7 V. If the curve is recorded from -1.7 V to -0.4 V and back to -1.7 V, i.e. if the oxidation in the anodic peak *B* has occurred no cathodic peak *D* can be observed. When comparing the curves with the corresponding ac. oscillograms ($dE/dt = f(E)$) an agreement can be observed: the only difference is a coincidence of the iodide incision with the anodic oxidation incision corresponding to the peak *B*.

A different behaviour was found with the N-n-butyl and N-n-pentyl derivative. These compounds also give the peaks *A*, *B*, J_0 , J_R but the change of *C* and *D* during the drop-life is more complicated. In the multi-sweep curve, however, at the beginning of the drop-life two anodic peaks, *C* and *C'* (at 0.78 and -0.9 V) result and going back to more negative potentials, two cathodic peaks *D* and *D'* (at -0.84 and -1.02 V): the polarisation occurs in the region from -1.7 V to 0.7 V and back to -1.7 V. As the mercury drop grows, the reduction peak *D'* gradually disappears; the peak *D* practically remains at its potential but toward the end of the drop-life a new cathodic peak *D''* results at -1.22 V. The whole effect on the oscillographic curve could be described as a kind of "rolling over" of the peaks. It seems that the fundamental pair of peaks is formed by *C* and *D* again. A certain analogy to the two oxidation peaks is the splitting of the anodic prewave *A* into a double-wave when working with the Kalousek commutator. If the polarisation proceeds from -1.7 V to -0.4 V and back to -1.7 V, i.e. if the region of oxidation is reached, the cathodic peaks *D*, *D'* and *D''* do not appear.

Oscillographic Polarography with Controlled Current

The whole pattern of the reduction and of the electrochemical activity of the reduction products obtained from the oscillographic function $dE/dt = f(E)$ with alternating current are in a good accordance, in particular with the single- and multi-sweep polarography, and with the Kalousek commutator. In this paragraph the potentials at which the incisions appear on the polarograms will not be expressed in volts but in the relative values *Q*.

It follows from a comparison of the curves obtained in absence and in presence of the studied substances (where the curve of the solution with the depolariser clearly extends beyond that of the blank both in the cathodic and the anodic branch, Fig. 5) that in all five substances both the oxidised form and the reduction products are adsorbed (in particular in the intermediate range of potentials) as can be also concluded from polarograms with superimposed alternating current. Added surface-active compounds, *e.g.* gelatin, occupy the electrode surface and displace the N-alkylpyridinium cations and their reduction products. The curves obtained in presence of the depolariser appear after such an addition within the contours of the curve of the blank.



FIG. 5

Oscillopolarograms with Controlled Current ($dE/dt = f(E)$)

$10^{-3}M$ N-methylpyridinium iodide in Britton-Robinson buffer pH 11.9. Thin line: curves of the supporting electrolyte, *a* without gelatin, *b* with $5 \cdot 10^{-3}\%$ gelatin.

In case of the N-methyl derivative (Fig. 5) the reduction manifests itself by an incision in the cathodic branch with $Q \approx 0.80$; this corresponds to the peak A on the single-sweep polarograms. In the anodic branch one can see only an indication of the incision corresponding to the peak C. On the other hand the incision with $Q \approx 0.32$, corresponding to the peak B, *i.e.* to the reoxidation of the reduction product, is quite clear. At very positive potentials an indistinct undulation appears approximately in the region of the electrode processes of iodides and of their salts with mercury.

The N-ethyl derivative differs from the preceding substance by the formation of a large anodic lobe; this points to a stronger adsorption of the reduction product which is formed at a somewhat more positive potential than in the above case. Such a more distinct adsorption, especially of the product, is characteristic with all other homologues. Here the splitting of the anodic incision at $Q = 0.30$ to 0.33 is clearer, in agreement with commutator experiments. Otherwise, the number and the positions of the incisions described in the first homologue do not greatly differ in these substances.

DISCUSSION

The reduction of all five N-alkylpyridinium cations takes place irreversibly; this follows from ac. oscillopolarography, from single- and multi-sweep polarograms and from experiments with the Kalousek commutator. The log plot of the reduction waves

of the first three derivatives points to the fact that the primary radical formed in the reduction is deactivated by dimerisation. The polarographic curves are thus in agreement with the equation for a wave in which the electrode process is followed by dimerisation⁴:

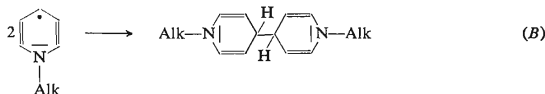
$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{\bar{i}^{2/3}}{\bar{i}_d - \bar{i}} \bar{i}^{1/3} + \frac{RT}{3nF} \ln \frac{ck_2t_1}{1.51}. \quad (2)$$

The half-wave potential of such a wave is given by the following formula:

$$E_{1/2} = E^{\circ} - 0.36 \frac{RT}{nF} + \frac{RT}{3nF} \ln ck_2t_1. \quad (3)$$

One may further conclude that the half-wave potential is a function of concentration c of the studied substance, of the rate constant k_2 of dimerisation and of the drop-time t_1 . An increase in concentration c or drop-time t_1 by one order should consequently cause a shift of the half-wave potential by 19 mV to less negative values. The formation of a maximum and adsorption effects on the curves of the five cations rendered impossible an investigation of the function $E_{1/2} = f(c)$. With controlled drop-time t_1 the shifts of the half-wave potential grow from 25 mV to about 35 mV per order for the series from N—CH₃ to N-n-C₅H₁₁. This result confirms again either an incomplete reversibility of the reaction or a deformation of the curve by adsorption phenomena. The quantitative disagreement with Mairanovskii's results² may also bear connection with the fact that Mairanovskii's compound possessed a different anion than iodide and, moreover, the composition of the solution was different: thus the conditions of adsorption were probably not identical. The dependence of $E_{1/2}$ on temperature showed that the oxidation of the primary product is irreversible since with increasing temperature $E_{1/2}$ of the commutated anodic waves is shifted to more negative potentials.

Basing on the experimental results we propose the following mechanism for the primary electrode process and the initial follow-up reaction:

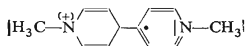


The dimerisation according to (B) occurs in such way that a prevalently a 4,4'-derivative results and not a 2,2' or 2,4'-dimer; this is in agreement with the quantum-chemical calculations about the significance of the π -electron septet in the chemistry of pyridine^{12,13}. The product formed in reaction (B) reacts further, both chemically and electrochemically. The follow-up reactions do not become evident on the polarographic curves; for this reason the value of n obtained with a dropping mercury electrode is very near to one. An exception is the N-methyl and N-ethyl derivative: both these dimerise so quickly that the follow-up reaction manifests itself even under these conditions by an increase of n to 1.28 or 1.21.

Markedly different is the situation with a stirred large-area mercury electrode. Here the dimerisation and the electrochemical activity both of the dimer and of the further products can play a decisive role. The apparent number of electrons from coulometric measurements with such an electrode depends chiefly on the rate of dimerisation of the primary reduction product. The coulometric measurements with a mercury-pool electrode for the three higher homologues prove that the rate of dimerisation is relatively slow here. The N-methyl and N-ethyl derivative occupy a special position: the reactivity of the primary radical is here very high, this being in accordance with preparative electrolyses and with spectral measurements.

From our experiments with blocking the follow-up radical reaction we found — in accord with our idea about the character of primary radical — that a single molecule of ascorbic acid reacts with two radicals. The fact that the decrease in height of the anodic wave of ascorbic acid does not amount to exactly one half of the decrease in the height of the reduction wave of the N-alkylpyridinium cation is probably caused by comparable rates of dimerisation and the interaction between ascorbic acid and the radical.

A key intermediate in all subsequent chemical and electrochemical reactions is here (in a similar manner as in the electrochemistry of quaternary 4,4'-bipyridylum salts) a viologen radical of the type



Its presence in the solution is revealed by an intensely blue coloration of the solution and a typical UV spectrum. The electrochemical properties of N-alkylpyridinium cations are profoundly affected by adsorption effects caused either by themselves or by their reduction products. In aqueous solutions adsorptivity is visible in the formation of streaming maxima caused evidently by adsorption of the primary reduction product on the mercury surface; a proof of adsorption was given in particular by ac.

polarography. It is very clear in the depolariser itself and increases with the length of the alkyl chain. The proof of adsorption of the product is not quite unambiguous by this method because the reduction proceeds at rather negative potentials. More convincing are the measurements with a hanging mercury drop. A strong adsorption of the depolariser and, in part, of the products was confirmed by ac. oscillographic polarography and in some measurements with the Kalousek commutator. In the latter case we arrived at the conclusion that the adsorption of the products of the higher homologues may occur in two different orientations.

Owing to adsorption the correlation between the half-wave potential of the first three N-alkylpyridinium cations and the substituent constants of the individual alkyl groups was not successful. With increasing length of the chain, $E_{1/2}$ of the reduction wave of N-alkylpyridinium cations is shifted: in a Britton–Robinson buffer with 20% dimethylformamide the shift occurs to less negative values, in the same buffer with 75% dimethyl sulfoxide the half-wave potentials shift in the opposite direction. According to the modified Taft equation¹⁴

$$\Delta E_{1/2} = \rho_{\pi, \text{het}}^* \cdot \sigma_{\text{CH}_2\text{X}} \quad (4)$$

the shift of $E_{1/2}$ in comparison with a standard (in which $\text{X} \equiv \text{H}$) should be negative if the reaction constant $\rho_{\pi, \text{het}}^* = 0.22$ (quotation¹⁵) and if the substituent constants given for all five alkyl groups in the literature are negative. The opposite direction of the shift in the solution with 80% water is ascribed to the adsorption of the primary product on the dropping mercury electrode; this adsorption cannot be suppressed by the presence of 20% dimethylformamide. However, the presence of 75% dimethylsulfoxide changes the direction of the shift of $E_{1/2}$. Making use of the following substituent constants $\sigma_{\text{CH}_2\text{X}}$: ethyl -0.10 ; n-propyl -0.11 ; n-butyl -0.13 ; n-pentyl -0.16 , one can compare the experimental shift of $E_{1/2}$ (in relation to $E_{1/2}$ of the N-methylpyridinium cation) with the theoretical shift obtained from equation (4):

Substituent	C_2H_5	C_3H_7	C_4H_9	C_5H_{11}
$E_{1/2, \text{theor}}$, mV	15	25	30	50
$E_{1/2, \text{exp}}$, mV	25	24	29	35

The incomplete agreement between theoretical and experimental data must be again ascribed to the adsorption of the product on the dropping mercury electrode. In order to obtain more precise results a corrected equation should be applied instead of (4); this would also regard the sterical effect of the substituents. Such an equation has not been applied, because an investigation with a greater number of substituents should be carried out which more strongly differ in their volumes; only then the sterical effect would appear in the experimental dependence $E_{1/2} = f(\sigma)$.

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Translated by the author (J. V.).